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1H AND 13C FOURIER TRANSFORM NMR CHARACTERIZATION OF JET FUELS --ETC(U)

1980 H C DORN

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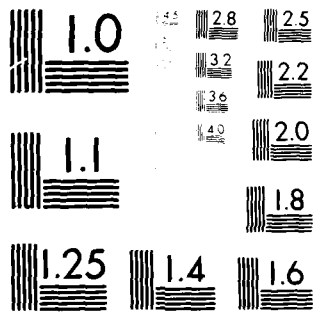
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(6) ^{17}H and ^{13}C Fourier Transform NMR Characterization
of Jet Fuels Derived From Alternate Energy Sources. ①

Six Month Progress Report

For The Period

April, 1980 - Sept., 1980

⑨ Progress rept. Apr-Sep 80.

10 H. C. / Dorn

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WORK STATEMENT

Characterization of Jet and Diesel Fuels by Nuclear Magnetic Resonance

This report discusses LC-Superscript 1 H LC-Superscript 1 H

- 1) Explore ~~LC-1 H~~ ^{LC-1 H} NMR studies from semi-preparative to analytical column size in order to establish ultimate chromatographic resolution conditions. (See Section I of this Report) Superscript 1 H

- 2) Explores quantitative approaches for ~~LC-1 H~~ ^{LC-1 H} NMR including a dual effluent stream to allow introduction of a quantitative reference before the ~~LC-1 H~~ ^{LC-1 H} NMR detector. Explores quantitative and ultimate sensitivity limits for the present ~~LC-1 H~~ ^{LC-1 H} NMR LC detector including optimization of ~~LC-1 H~~ ^{LC-1 H} NMR insert for ~~LC-1 H~~ ^{LC-1 H} LC-Superscript 1 H NMR. (See Section I of this Report) LC-Superscript 1 H

- 3) Provides ~~LC-1 H~~ ^{LC-1 H} NMR data profiles for 10 synthetic mixtures and corresponding analytical data (e.g., total %H, %H, aromatic, %H aliphatic, %n-alkanes and branched alkanes, %alkyl aromatics and substituted naphthalenes). (See Section II of this Report) LC-Superscript 1 H

- 4) Provide ~~LC-1 H~~ ^{LC-1 H} NMR data profiles for 30 middle distillate fuels and corresponding analytical data (see 3 above). LC-Superscript 1 H

- 5) Provides static ~~LC-1 H~~ ^{LC-1 H} NMR and ~~LC-1 H~~ ^{LC-1 H} NMR quantitative data for 45 middle distillate fuels. At least six of these samples will be diesel fuel marine. (See Section III of this Report). LC-Superscript 1 H

- 6) Provides static ~~LC-1 H~~ ^{LC-1 H} NMR and ~~LC-1 H~~ ^{LC-1 H} NMR quantitative data for 20 synthetic mixtures of hydrocarbons. (See Section II of this Report). LC-Superscript 1 H

Title		LC-Superscript 1 H	
Author		LC-Superscript 1 H	
Date		LC-Superscript 1 H	
Availability Codes		LC-Superscript 1 H	
Accession Number		LC-Superscript 1 H	
Indexing Terms		LC-Superscript 1 H	
Abstract		LC-Superscript 1 H	
Notes		LC-Superscript 1 H	
References		LC-Superscript 1 H	
Other		LC-Superscript 1 H	
A		LC-Superscript 1 H	

SECTION I

The flow LC- ^1H NMR studies of jet fuels until Sept., 1980 utilized a modified Jeol PS-100 as previously described.^{1,2} The acquisition of new liquid chromatography columns (Whatman Partisil M9 10/25 and Whatman Partisil M9 10/25 PAC) in May, 1980 provided much better chromatographic performance than the previously utilized Merck Silica Gel 60 Size B column. An illustration of the performance of one of the new columns (Whatman Partisil M9 10/25 PAC) is given in Figure 1 which is a partial LC- ^1H NMR profile of a synthetic mixture. This profile focuses attention on only the profile region where n-butylbenzene, m-xylene and tetralin have very similar elution. In fact, the refractive index detector indicates only one peak for this chromatographic elution volume. However, the LC- ^1H NMR profile clearly separates the elution pattern of n-butylbenzene (files 15 to 18), m-xylene (files 18 to 20) and finally tetralin (files 21 to 23).

In addition, a double tuned $^1\text{H}/^{19}\text{F}$ circuit was built for this instrument to allow a magnetic field lock for the internal fluorine containing solvents (e.g., trichlorotrifluoroethane). Numerous other NMR insert designs were also tried. However, the best resolution and (S/N) achieved for this flow ^1H -LCNMR instrument was ~ 2.8 Hz and $\sim 20/1^*$, respectively. Although this was significantly better than the performance reported in our initial paper,² the relatively low (S/N) limited extension to truly analytical chromatographic columns.

*) 1% ethylbenzene, standard (S/N) test for ^1H NMR.

The acquisition of our new Supercon FX-200 in September, 1980 immediately became the focal point for this portion of the study. We purchased a probe housing for this instrument and modified it for the flow LC-¹H NMR studies. Although it took 3-4 months to develop a reliable insert design, we have recently obtained resolution of 1.6 Hz and a (S/N) of 200/1 at a flow rate of 1 ml/minute. The order of magnitude improvement in (S/N) should allow better data for items 1, 2 and 4 of the work statement even though considerable experimental time was necessary in developing this approach for the Supercon FX-200 instrument. We are now prepared to complete items 1, 2 and 4 in the work statement of the contract utilizing the Supercon FX-200 instrument. This phase of the study should be completed in the next six months.

SECTION II

Studies of Synthetic Mixtures

As previously indicated in our preliminary studies of synthetic mixtures,^{1,3} the major focal point should be to ascertain precisely which molecular parameters influence smoke points and freezing points. To this end, we have prepared stock synthetic mixtures #1 (previously discussed, see ref. 3). More recently, a new stock synthetic mixture #1A was prepared. The composition of these stock solutions are fairly similar and are given in Tables 1 and 2. To a portion of these stock solutions (#1 and #1A) we have systematically added a single compound to

prepare a number of new synthetic mixtures. For example, samples #2-5 were prepared by addition of 1.34, 2.68, 5.36 and 10.72 g of n-butylbenzene, respectively, to 27.49 g of stock solution #1. To date, seventeen separate compounds have been studied with usually four concentrations of each component. This data is presented in Figures 2 and 18 with smoke points determined by ASTM procedures^{1,3} plotted versus the mole fraction of each component in question. In Table 3, the slopes and correlation coefficient for each compound are also presented.

From this data, it is readily apparent that the alkyl-aromatics in particular have drastically lower smoke points. Furthermore, it appears from the limited data that the degree of alkyl substitution on the aromatic ring is a major factor controlling smoke points. This data is summarized below with the slopes from Table 3 in parenthesis.

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AROMATICS

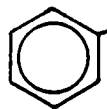


(-21.8)

MONO-ALKYL-
AROMATICS

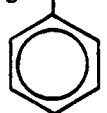


(-37.3)



(CH₂)₃-CH₃
(-31.0)

CH₃-CH-CH₃

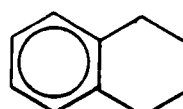


(-33.8)

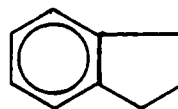
DI-ALKYL-
AROMATICS



(-52.4)



(-47.3)



(-46.7)

The only possible exception to this trend is naphthalene (slope -31.2), however, it should be noted that solubility limited a complete study of naphthalene as a solute in stock solution #1. It would probably be advantageous to utilize α or β methylnaphthalene as solutes where solubility is probably not a limitation. In addition, compounds with tri or tetra alkyl substitution on an aromatic ring, for example, mesitylene and 1,2,3,4-tetramethylbenzene, respectively, should also be utilized as solutes.

The linear and branched alkanes have slopes which are positive and represent a class which increase the smoking point with increasing concentration. The only exception is pentane (slope -14.4). We do not know the reason for this discrepancy for pentane, but it could be related to the high volatility of pentane. It should be noted that both n-pentane and n-hexane have very poor correlation coefficients (see Table 3). The slopes for the other seven alkanes examined to date superficially appear to belong to one class with slopes which ranges from +4.4 to +26.2.

From the data above, it appears possible to predict smoke points with an equation of the following general form.

$$\text{smoke point(mm)} = \left[(m_{aa}) \left(\frac{C_{ar} - H_{ar}}{C_T} \right) + k_{aa} \right] x_{aa} + m_a x_a + k_o \quad 1)$$

In this equation, we assume that two chemical classes must be separately treated to account for smoke points in fuels, namely, alkylaromatics and alkanes. The m_a and x_a values represent the approximate average slope constant and mole fraction, respectively, for alkanes. The m_a value would be approximately +15 obtained from the synthetic model studies where the slopes ranged from +4.4 to 26.2. Thus, we assume one average slope value for all alkanes in these synthetic mixtures. The k_o constant is the average intercept for the alkanes and alkylaromatics ($\sim +39$, see Table 3). The $(\frac{C_{ar}-H_{ar}}{C_T})$ parameter directly reflects the degree of substitution on aromatic rings which in turn lowers smoke points. This is clearly indicated by the synthetic model work in this report and a previous report.¹

Although carbon aromaticity (f_a) might be employed in this equation, we feel that the $(\frac{C_{ar}-H_{ar}}{C_T})$ parameter has inherent virtues. For example, a comparison of n-butylbenzene and tetralin would yield the same f_a value (0.6) whereas, the $(\frac{C_{ar}-H_{ar}}{C_T})$ parameter would have values of 0.1 and 0.2, respectively. The latter is consistent with the substantially different slopes for these compounds (-31.0 and -47.3, respectively). The m_{aa} value (~ -139.5) was obtained from a plot of the slopes for all alkylaromatics in the synthetic model study (see Figure 19) versus the $(\frac{C_{ar}-H_{ar}}{C_T})$ value appropriate for each added alkylaromatic. The k_{aa} value (~ -17.6) is the intercept obtained from the plot described above. It should be noted that this value is in reasonably good agreement with the measured value for benzene

$(\frac{C_{ar}-H_{ar}}{C_T} = 0, \text{ slope} = -21.77, \text{ Table 3})$. The remaining parameter is x_{aa} the mole fraction of alkylaromatics.

Thus, for a given fuel or synthetic model mixture the unknown variables to determine smoke points by the equation above are x_{aa} , x_a and $(\frac{C_{ar}-H_{ar}}{C_T})$. These variables can be obtained from the static 1H and ^{13}C NMR measurements for a given fuel, however, LC- 1H NMR measurements would probably be necessary to obtain better values of x_{aa} and x_a . In any case, we plan to explore the use of equations of the type indicated above to predict smoke points of synthetic mixtures and jet fuels. The LC- 1H NMR, 1H and ^{13}C static NMR measurements for the synthetic mixtures have not been completed at this time, however, the work described above is a necessary prelude to actually obtaining this experimental data. We anticipate completion of this portion of the study during the next three months.

SECTION III

1H and ^{13}C Static FT NMR Studies of Fuels

In this phase of the work ~45 new fuel samples were studied using the quantitative 1H and ^{13}C FT NMR approaches previously described.^{1,3} In addition, smoke points and freezing points^{1,3} were determined for each fuel sample (Table 4). The NMR instrument utilized for each measurement is also indicated in this Table. The carbon aromaticity values and hydrogen aromaticities were obtained directly from the ^{13}C and 1H NMR spectra, respectively. The $(\frac{C_{ar}-H_{ar}}{C_T})$ values were obtained from the NMR data and elemental combustion data provided for these samples.

In Figures 20 and 21, the carbon aromaticity and $(\frac{C_{ar}-H_{ar}}{C_T})$ parameters are correlated with the smoke point data for these fuels. The correlation coefficients for these two plots are very similar -0.839 and -0.840, (45 samples for each plot) respectively. This suggests that both NMR parameters are equally efficient in correlating smoke points of fuels. The carbon aromaticity correlation appears to be somewhat better than data previously obtained for other fuels in this study (see Figure 2, p. 24 of reference 1). However, it should be noted that most fuels in this report have carbon aromaticities greater than .05 to .10 which was not true of earlier fuels employed in this study.^{1,3}

In sharp contrast, the much poorer correlation of hydrogen aromaticity with smoke points (Figure 22, correlation coefficient -0.747) suggests that carbon aromaticity and/or $(\frac{C_{ar}-H_{ar}}{C_T})$ parameters are better indicators of smoking points of a given fuel. Since hydrogen aromaticity only indicates aromatic carbon which is unsubstituted (C_u)*, the better correlation with carbon aromaticity and $(\frac{C_{ar}-H_{ar}}{C_T})$ clearly indicates the importance of substituted aromatic carbon (C_s and C_s').* This is also consistent with the results obtained in the synthetic model studies (See Section I).

As indicated above, most of the work in this phase of the study is completed. However, we plan to recheck several of the values reported in Table 4. A more complete examination of this data and other possible correlations will be presented in the Final Report of this study.

*) See final report (period-March, 1978-Aug., 1979) for a more complete description of these parameters.

TABLE 1

Stock Mixture #1

<u>Compound</u>	<u>M.W.</u>	<u>Grams</u>	<u>Moles (n)</u>	<u>Mole Fraction (X_i)</u>
n-butylbenzene	134.22	13.45	0.1002	0.02273
m-xylene	106.17	10.12	0.0953	0.02162
tetralin	132.21	13.08	0.0989	0.02243
naphthalene	128.17	12.80	0.09987	0.02265
dodecane	170.34	85.64	0.5026	0.1140
isooctane	114.23	200.41	1.7544	0.3979
hexane	86.18	43.65	0.5065	0.1148
n-nonane	128.26	95.71	0.7462	0.16935
hexadecane	226.45	56.50	0.2495	0.05659
n-pentane	72.15	<u>18.43</u>	<u>0.2554</u>	<u>0.05793</u>
TOTAL		549.79	4.4089	1.00000

TABLE 2

STOCK MIXTURE #1A

<u>Compound</u>	<u>M.W.</u>	<u>Grams</u>	<u>Moles (m)</u>	<u>Mole Frac (x_i)</u>
n-butylbenzene	134.22	13.25	0.0987	0.02273
m-xylene	106.17	10.14	0.0955	0.02199
tetralin	132.21	13.08	0.0989	0.02277
naphthalene	128.17	12.80	0.0999	0.02300
dodecane	170.34	85.67	0.5029	0.11580
isooctane	114.23	200.40	1.7540	0.40387
hexane	86.18	43.65	0.5065	0.11662
n-nonane	128.26	52.74	0.4112	0.09468
hexadecane	226.45	56.20	0.2482	0.05715
n-pentane	72.15	18.43	0.2554	0.05881
n-decane	142.29	38.67	0.2718	0.06258
Total		545.03	4.343	1.0000

TABLE 3

Slope, Intercept and Correlation Coefficient (Smoke Point Versus Mole Fraction) Data For Compounds Added to Synthetic Mixtures #1 and #1A*

Compound linear alkanes	Synthetic Mixture Used	Slope ($\frac{\text{smoke point (mm)}}{\text{mole fraction } x_i}$)	Intercept	Correlation Coefficient
n-pentane	1	-14.44	41.68	-0.838
n-hexane	1	+15.92	39.11	0.867
n-nonane	1	+26.18	36.36	0.996
n-undecane	1A	+ 5.62	40.78	0.977
n-dodecane	1	+13.65	39.62	0.982
n-hexadecane	1	+22.08	40.01	0.975
n-octadecane	1A	+21.17	40.74	0.979
<u>Branched Alkanes</u>				
isooctane	1	+ 4.35	39.19	0.921
<u>Alkenes</u>				
2-hexene	1A	+19.06	37.16	0.674
<u>Aromatics</u>				
benzene	1A	-21.77	43.40	-0.859
naphthalene	1	-31.19	33.62	-0.999
<u>Alkyl Aromatics</u>				
toluene	1A	-37.34	41.09	-0.978
cumene	1A	-33.79	37.64	-0.961
n-butylbenzene	1	-31.03	37.55	-0.994
m-xylene	1	-52.40	40.64	-0.982
tetralin	1	-47.26	35.29	-0.998
indan	1A	-46.65	29.92	-0.972

*) All data obtained from linear least squares program and plotted in Figures 2 to 18.

TABLE 4
Smoke Points, Freezing Points, ^1H and ^{13}C
FT NMR Data for Fuels 25-69

Sample	Source	Smoke ¹ Point	Freezing ² Point	Carbon ³ Aromaticity	Hydrogen ⁴ Aromaticity	$(\frac{C_{ar}-H_{ar}}{C_T})^5$
25	Naval Lab	11.8	-41.0	.312 (FX-60Q)	.106	-
26	Naval Lab	16.1	-47.0	.195 (FX-60Q)	.063	-
27	Naval Lab	16.6	-51.5	.192 (FX-60Q)	.054	-
28	Naval Lab	20.5	-42.0	.116 (FX-60Q)	.030	-
29	Naval Lab	17.5	-51.0	.184 (FX-60Q)	.051	-
30	Naval Lab	20	-52.0	.133 (FX-60Q)	.032	-
31	Naval Lab	18.0	-18.5	.148 (FX-60Q)	.039	-
32	Naval Lab	23.1	-41.0	.134 (FX-60Q)	.030	-
33	Naval Lab	19.7	-50.0	.156 (FX-60Q)	.042	-
34	Naval Lab	21.5	-47.5	.160 (FX-60Q)	.030	-
35	Naval Lab	17.2	-62.0	.168 (FX-60Q)	.062	-
36	Naval Lab	20.7	-48.0	.158 (FX-60Q)	.043	-
37	Naval Lab	16.3	-17.0	.159 (FX-200)	.037	-
38	Naval Lab	14.0	+12.0	.175 (FX-200)	.020	-
39	Air Force	7.0	-93.0	.665 (FX-200)	.304	.2550
40	Air Force	3.5 (3.9)*	-25.0	.770 (FX-60Q)	.448	.2853
41	Air Force	25.6 (23.1)*	-65.0	.104 (FX-60Q)	.025	.0533
42	Air Force	22.3 (21.7)*	-44.0	.101 (FX-200)	.030	.0424
43	Air Force	18.4 (17.7)*	-28.0	.100 (FX-60Q)	.031	.0404
44	Air Force	8.9 (9.9)*	-37.0	.348 (FX-60Q)	.139	.1226

Sample	Source	Smoke ¹ Point	Freezing ² Point	Carbon ³ Aromaticity	Hydrogen ⁴ Aromaticity	$(\frac{C_{ar}-H_{ar}}{C_T})^5$
45	Air Force	10.5(13.3)*	-48.5	.236(FX-60Q)	.090	.0745
46	Air Force	12.0(11.8)*	-55.0	.381(FX-60Q)	.150	.1337
47	Air Force	14.5(15.8)*	-40.0	.214(FX-60Q)	.085	.0620
48	Air Force	-	-	-	-	-
49	Air Force	12.0(11.8)*	-63.0	.277(FX-60Q)	.102	.0952
50	Air Force	11.0(11.3)*	-71.0	.404(FX-60Q)	.167	.1282
51	Air Force	13.5	-65.0	.303(FX-60Q)	.118	.0924
52	Air Force	22.6	-36.0	.146(FX-60Q)	.063	.0237
53	Air Force	13.0	-25.5	.220(FX-60Q)	.068	.0992
54	Air Force	31.1	-0.5	.058(FX-60Q)	.024	.0098
55	Air Force	27.6	-58.0	.146(FX-60Q)	.053	.0393
56	Air Force	23.6	-47.5	.098(FX-60Q)	.036	.0293
57	Air Force	9.5	-52.0	.408(FX-60Q)	.155	.1516
58	Air Force	13.5	-66.0	.287(FX-60Q)	.103	.0994
59	Air Force	16.0	-12.0	.179(FX-60Q)	.058	.0746
60	Air Force	9.0	-12.0	.342(FX-60Q)	.133	.1253
61	Air Force	27.5	-51.0	.080(FX-60Q)	.025	.0292
62	Air Force	21.5	-38.0	.138(FX-200)	.039	.0627
63	Air Force	25.8	-31.0	.087(FX-200)	.031	.0252
64	Air Force	18.4	-59.0	.239(FX-60Q)	.067	.1137
65	Air Force	24.8	-53.0	.105(FX-200)	.027	.0517

<u>Sample</u>	<u>Source</u>	<u>Smoke¹ Point</u>	<u>Freezing² Point</u>	<u>Carbon³ Aromaticity</u>	<u>Hydrogen⁴ Aromaticity</u>	<u>$\frac{C_{ar}-H_{ar}}{C_T}$⁵</u>
66	Air Force	10.9	-63.0	.420(FX-60Q)	.155	.1600
67	Air Force	27.8	-65.0	.058(FX-200)	.022	.0126
68	Air Force	28.3	-62.0	.112(FX-200)	.028	.0548
69	Air Force	20.4	-53.0	.123(FX-200)	.029	.0668

1) ASTM procedure D1322-75

2) ASTM procedure D2386-67

3) Aromatic carbon to total carbon ratio, NMR instrument utilized in ()

4) Aromatic hydrogen to total hydrogen ratio, same NMR instrument utilized

5) Values obtained from carbon and hydrogen aromaticity data with elemental combustion data provided by Major Don Potter, USAF

*) Repeated measurements of smoke point

TABLE 5
Fuel Code Identification

<u>Sample</u>	<u>Fuel Code</u>
25	PE-5-77
26	PE-6-77
27	PE-7-77
28	PE-8-77
29	PE-9-77
30	PE-84-79
31	PE-76-79
32	PE-171-79
33	PE-172-79
34	PE-173-79
35	PE-189-79 .
36	J22
37	Oil
38	Shale I-DFM
39-69	VN-80-39-VN-80-69

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1. Six Month Progress Report Prepared For the Naval Research Laboratory for the period Sept. 20, 1979-March 17, 1980
2. Haw, James F., Glass, T. E., Hausler, D. W., Motell, E. and Dorn, H. C., Anal. Chem., (1980) 52, 1135.
3. Final Progress Report Prepared For the Naval Research Laboratory for the period March 23, 1978-Aug., 30, 1979.

FIGURES

- Figure 1 Partial LC-¹H NMR Profile of Synthetic Mixture
Containing n-butylbenzene, m-xylene and tetralin
- Figure 2 Smoke Point vs. Mole Fraction of n-Pentane added
to Synthetic Mixture 1
- Figure 3 Smoke Point vs. Mole Fraction of n-Hexane added
to Synthetic Mixture 1
- Figure 4 Smoke Point vs. Mole Fraction of n-Nonane added
to Synthetic Mixture 1
- Figure 5 Smoke Point vs. Mole Fraction of n-Undecane added
to Synthetic Mixture 1A
- Figure 6 Smoke Point vs. Mole Fraction of n-Dodecane added
to Synthetic Mixture 1
- Figure 7 Smoke Point vs. Mole Fraction of n-Hexadecane
added to Synthetic Mixture 1
- Figure 8 Smoke Point vs. Mole Fraction of n-Octadecane
added to Synthetic Mixture 1A
- Figure 9 Smoke Point vs. Mole Fraction of Isooctane
added to Synthetic Mixture 1
- Figure 10 Smoke Point vs. Mole Fraction of 2-Hexene
added to Synthetic Mixture 1A
- Figure 11 Smoke Point vs. Mole Fraction of Benzene
added to Synthetic Mixture 1A
- Figure 12 Smoke Point vs. Mole Fraction of Naphthalene
added to Synthetic Mixture 1
- Figure 13 Smoke Point vs. Mole Fraction of Toluene added
to Synthetic Mixture 1A
- Figure 14 Smoke Point vs. Mole Fraction of Cumene added
to Synthetic Mixture 1A
- Figure 15 Smoke Point vs. Mole Fraction of n-Butylbenzene
added to Synthetic Mixture 1
- Figure 16 Smoke Point vs. Mole Fraction of m-Xylene added
to Synthetic Mixture 1
- Figure 17 Smoke Point vs. Mole Fraction of Tetralin added
to Synthetic Mixture 1

- Figure 18 Smoke Point vs. Mole Fraction of Indan added to Synthetic Mixture 1A
- Figure 19 Slopes of Alkylaromatics versus $(\frac{C_{ar}-H_{ar}}{C_T})$ Parameter
- Figure 20 Plot of Carbon Aromaticity (^{13}C NMR) versus Smoke Points for Fuels 25-69
- Figure 21 Plot of $(\frac{C_{ar}-H_{ar}}{C_T})$ Parameter versus Smoke Points for Fuels 25-69
- Figure 22 Plot of Hydrogen Aromaticity (1H NMR) versus Smoke Points for Fuels 25-69

FIGURE 1

LC-¹H NMR
PROFILE OF
MODEL MIXTURE
(n-BUTYL BENZENE, m-XYLENE
and TETRALIN REGION)

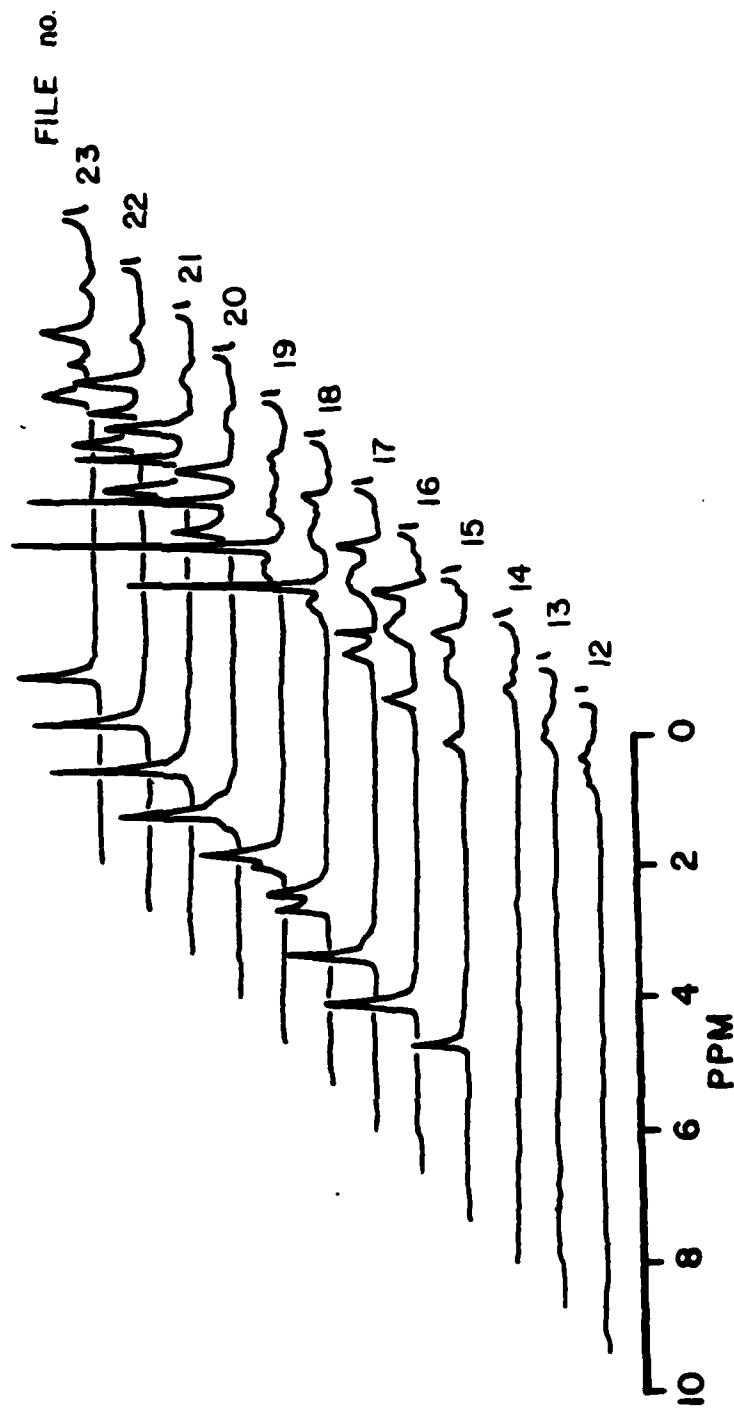
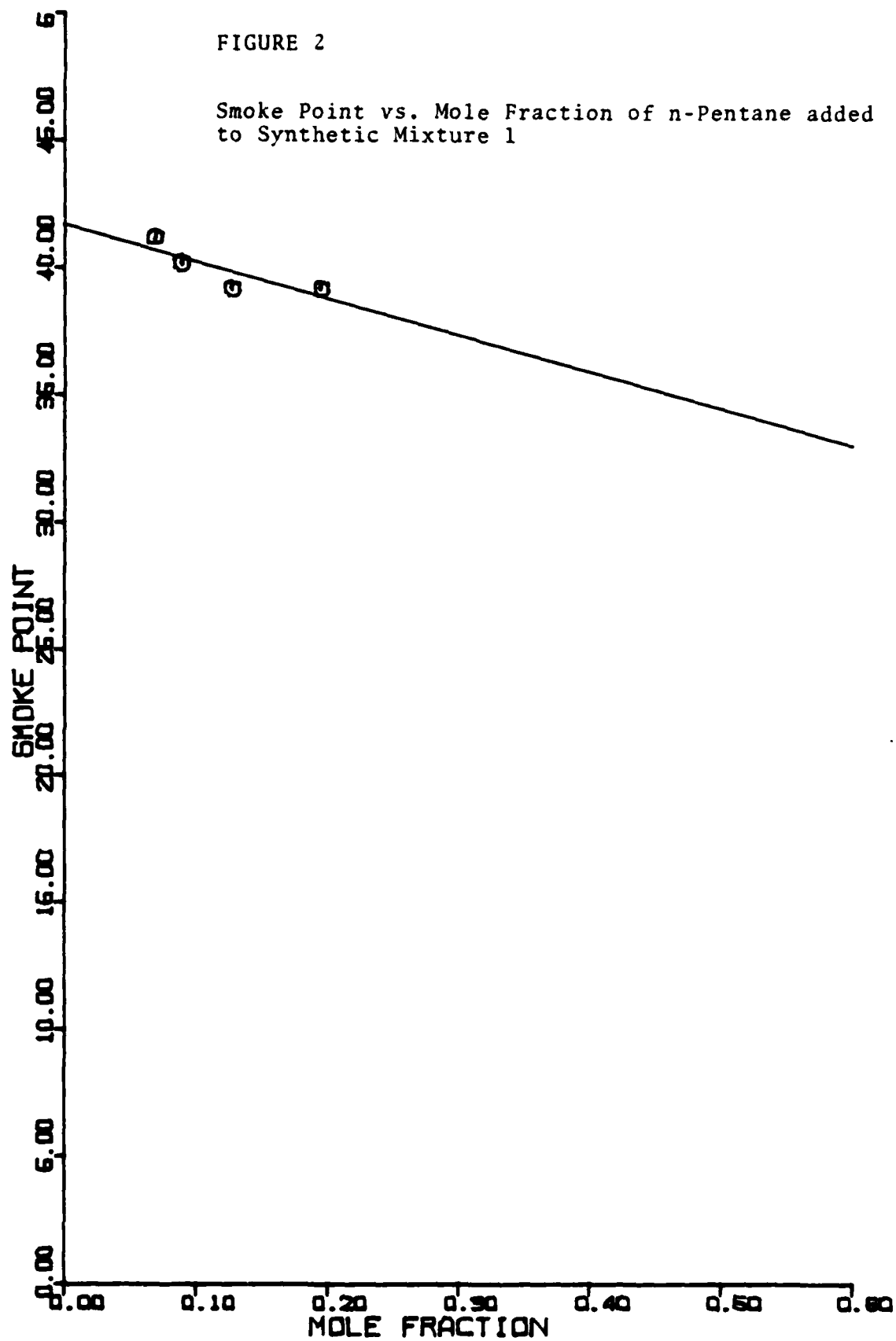


FIGURE 2

Smoke Point vs. Mole Fraction of n-Pentane added
to Synthetic Mixture 1



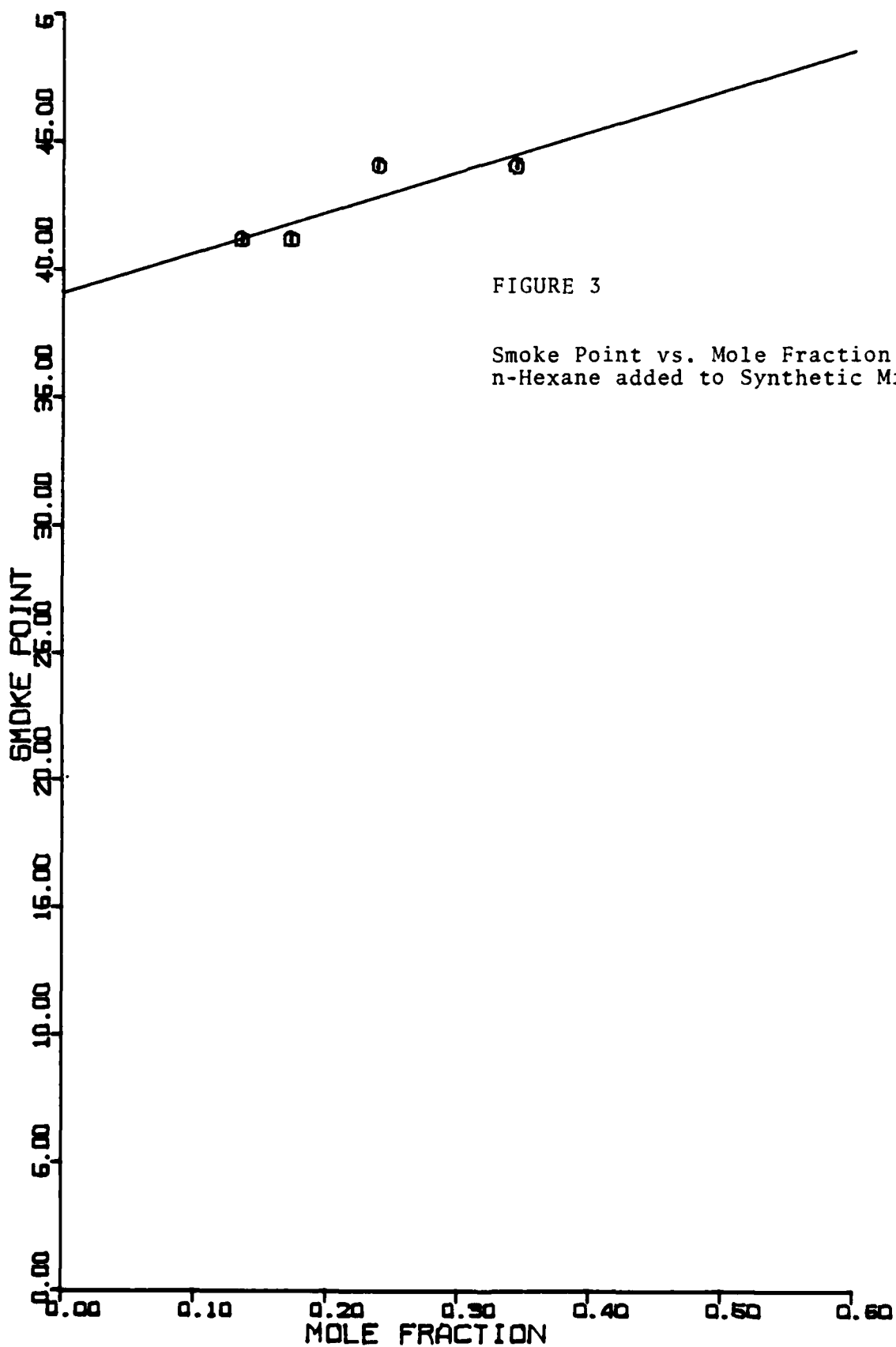


FIGURE 3

Smoke Point vs. Mole Fraction of
n-Hexane added to Synthetic Mixture 1

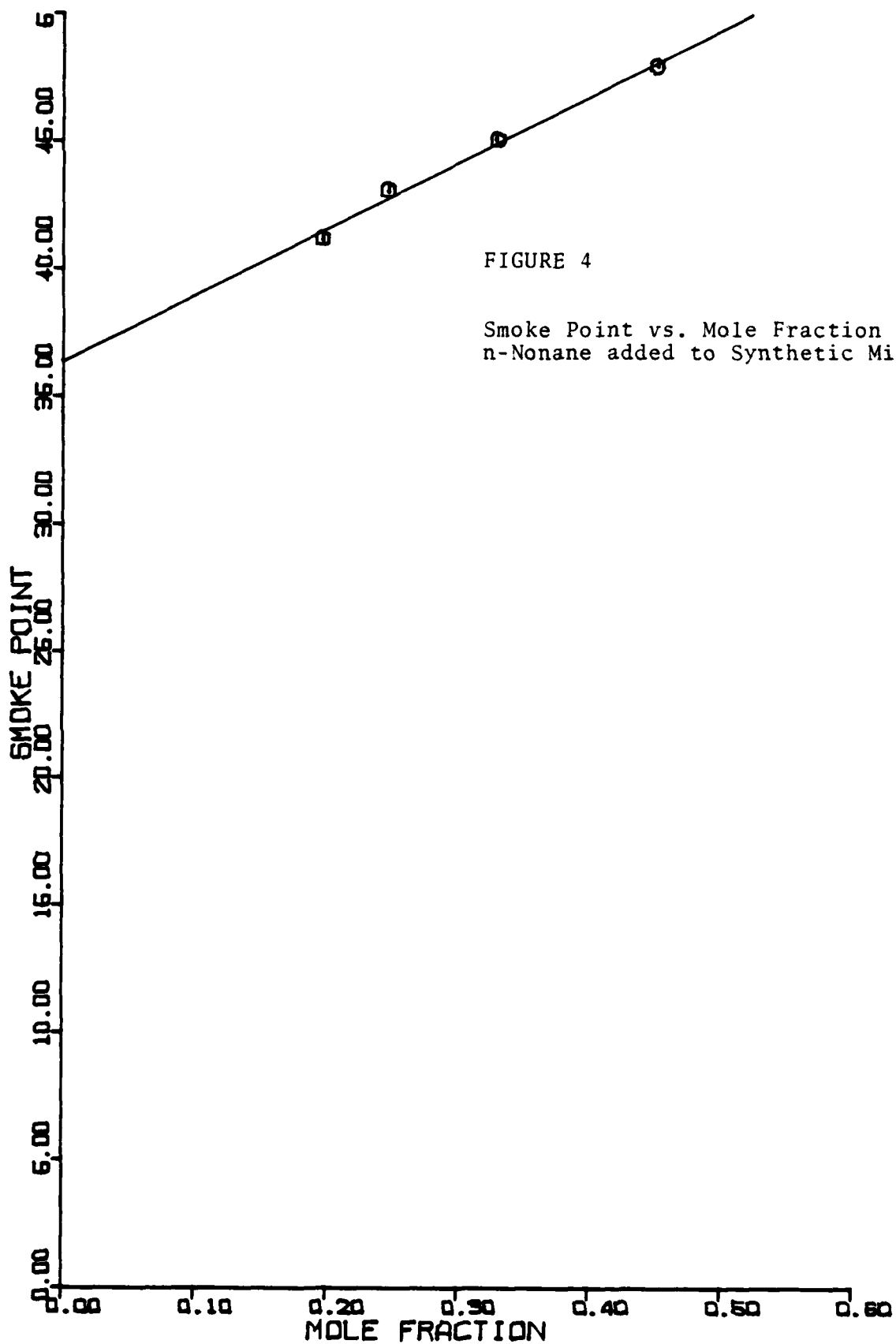


FIGURE 4

Smoke Point vs. Mole Fraction of
n-Nonane added to Synthetic Mixture 1

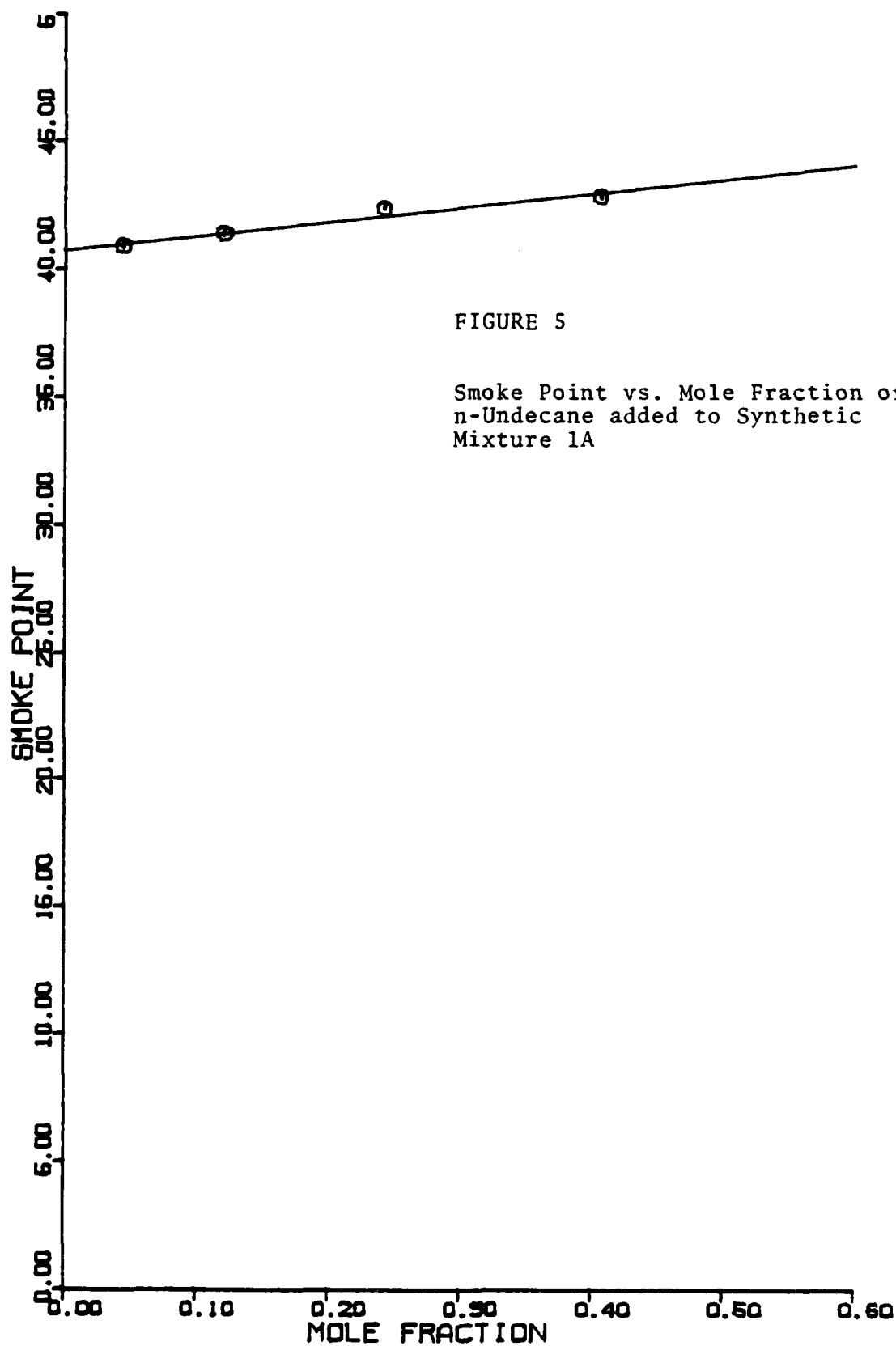


FIGURE 5

Smoke Point vs. Mole Fraction of
n-Undecane added to Synthetic
Mixture 1A

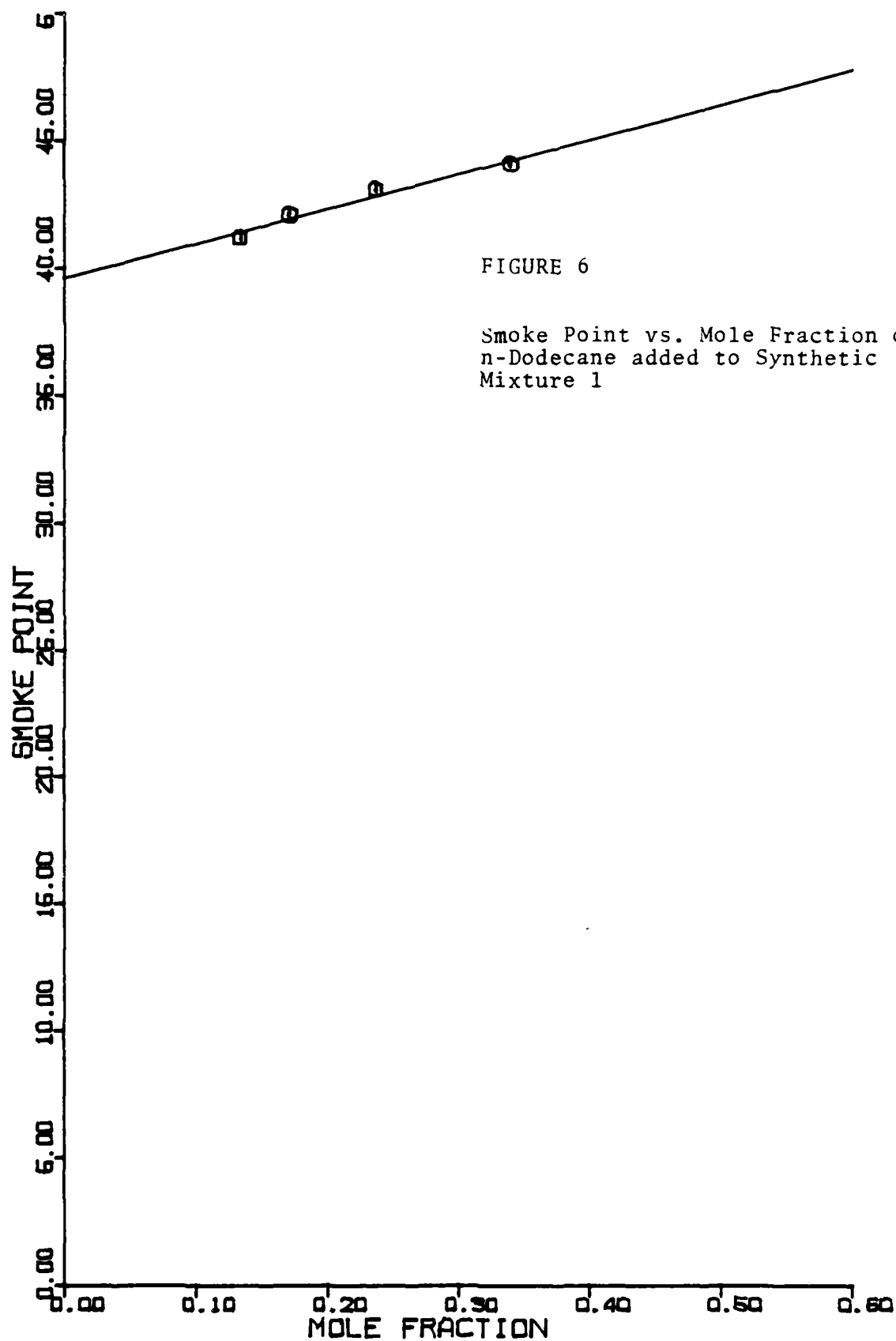


FIGURE 6

Smoke Point vs. Mole Fraction of
n-Dodecane added to Synthetic
Mixture 1

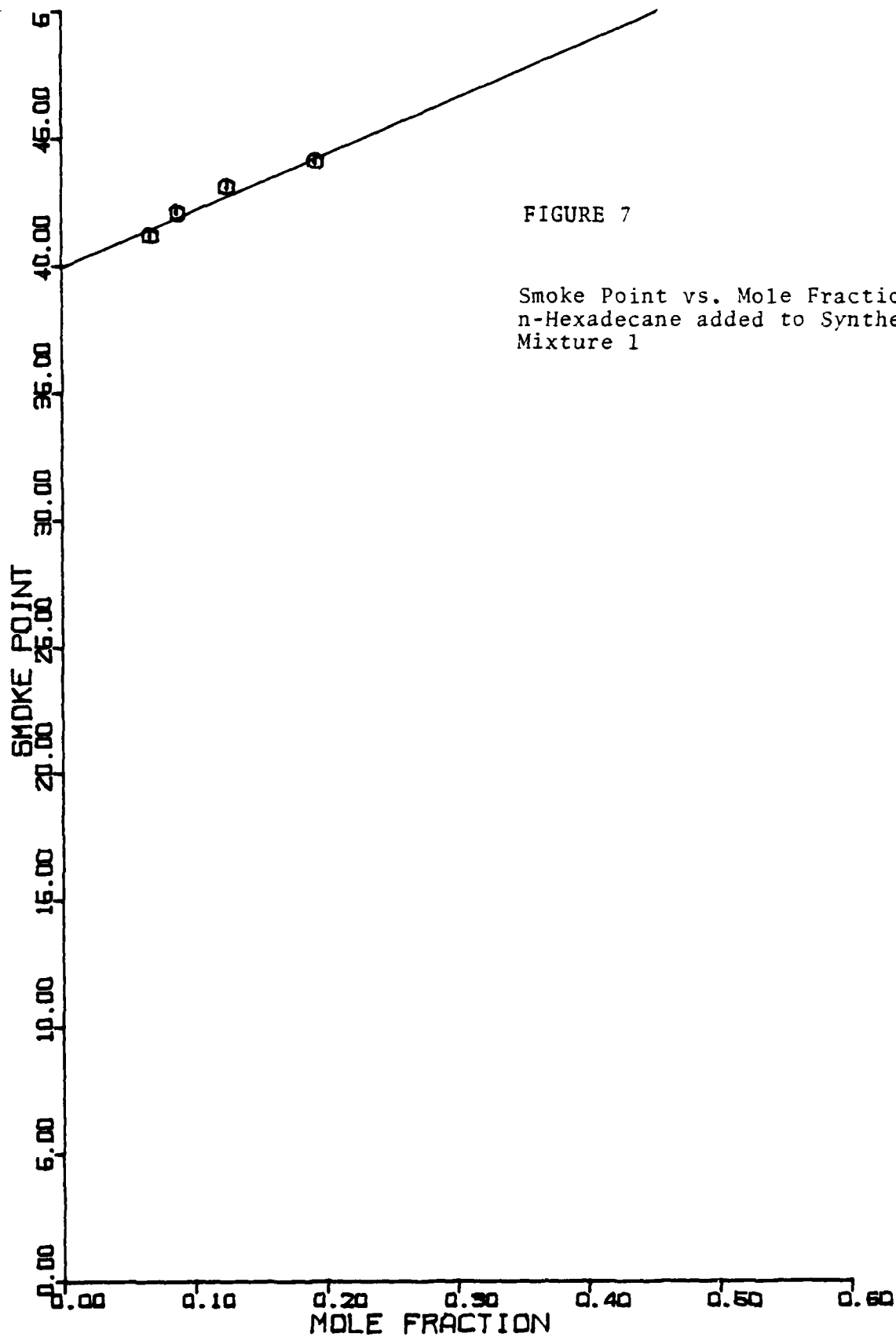


FIGURE 7

Smoke Point vs. Mole Fraction of
n-Hexadecane added to Synthetic
Mixture 1

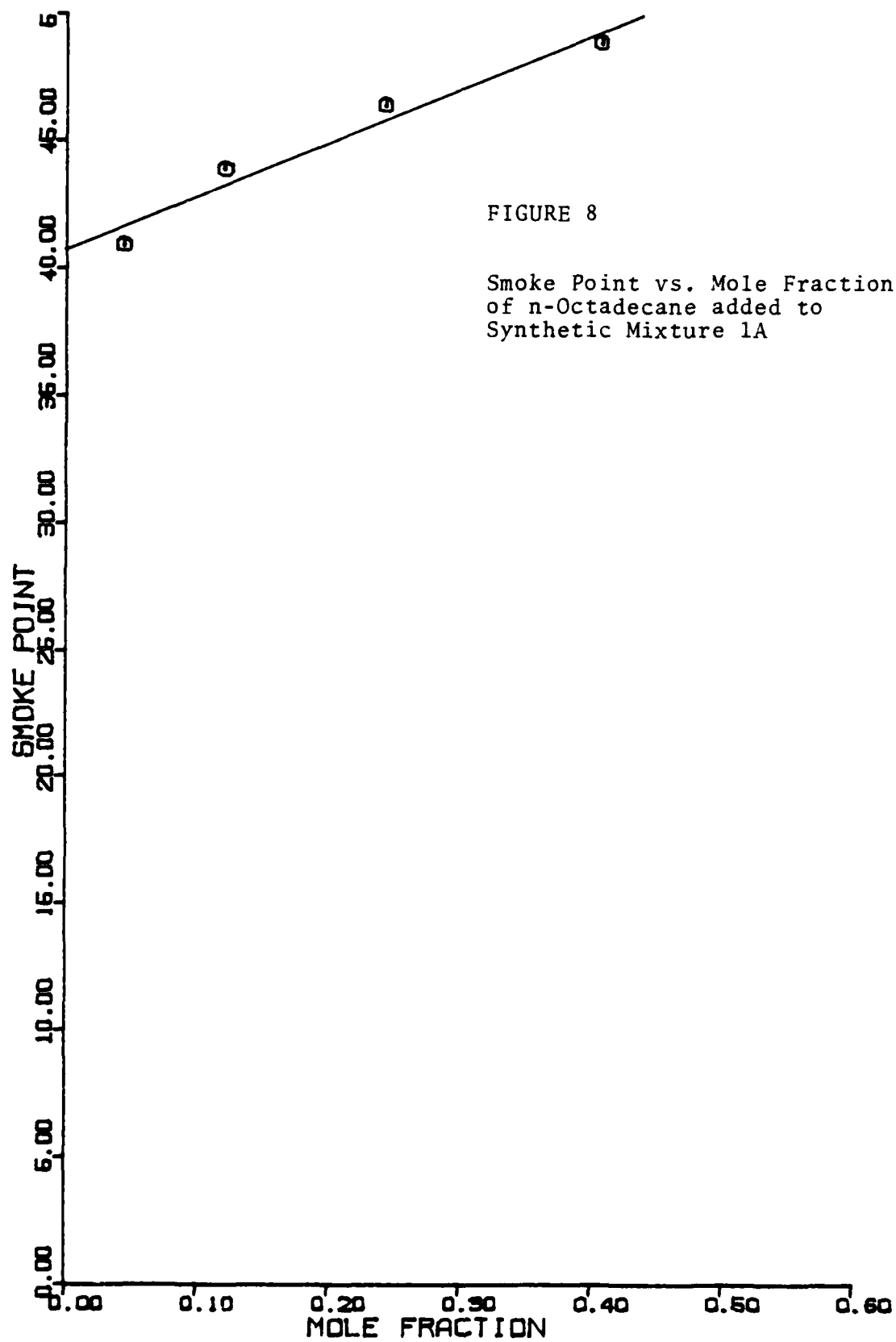


FIGURE 8

Smoke Point vs. Mole Fraction
of n-Octadecane added to
Synthetic Mixture 1A

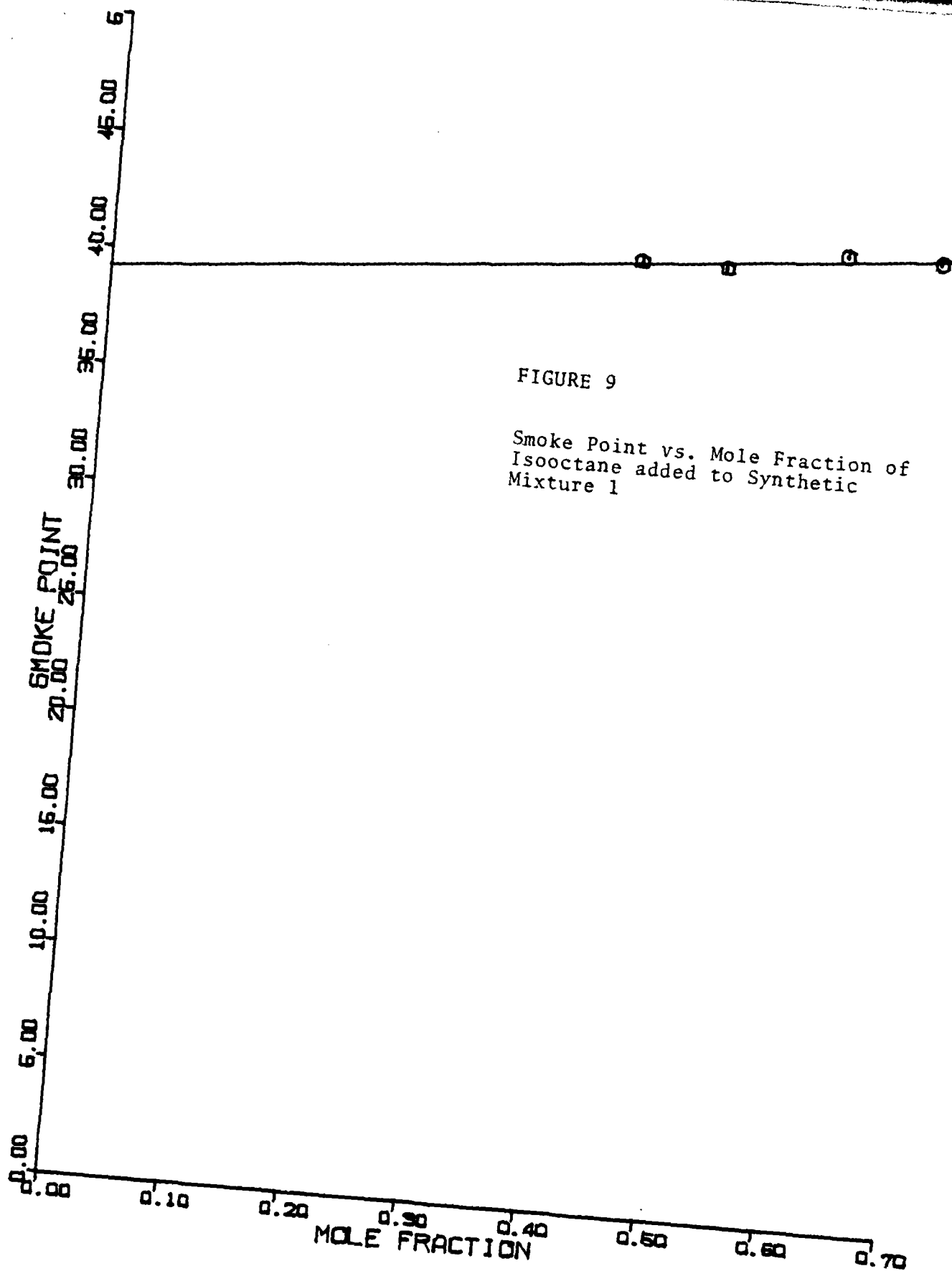


FIGURE 9

Smoke Point vs. Mole Fraction of
Isooctane added to Synthetic
Mixture 1

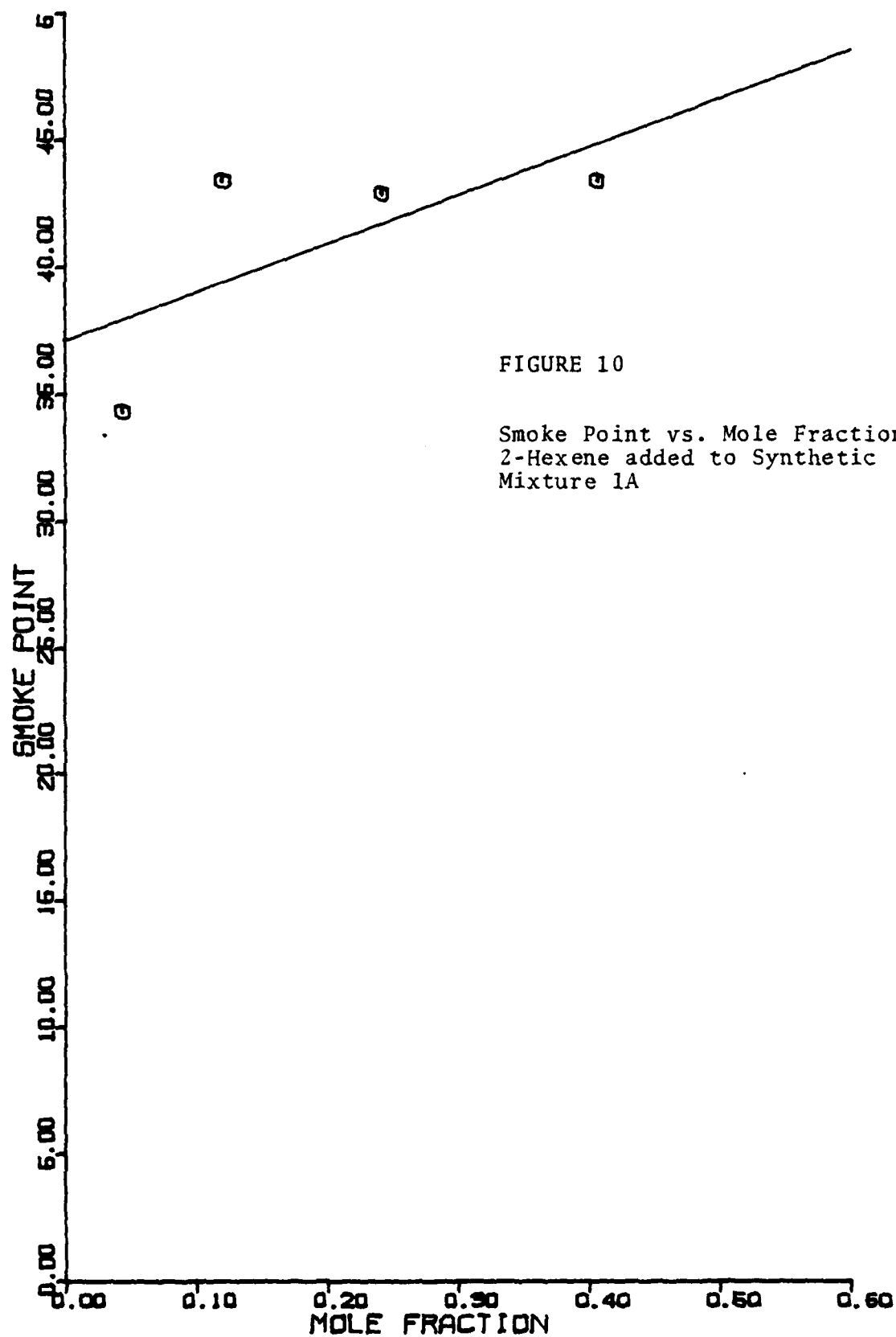
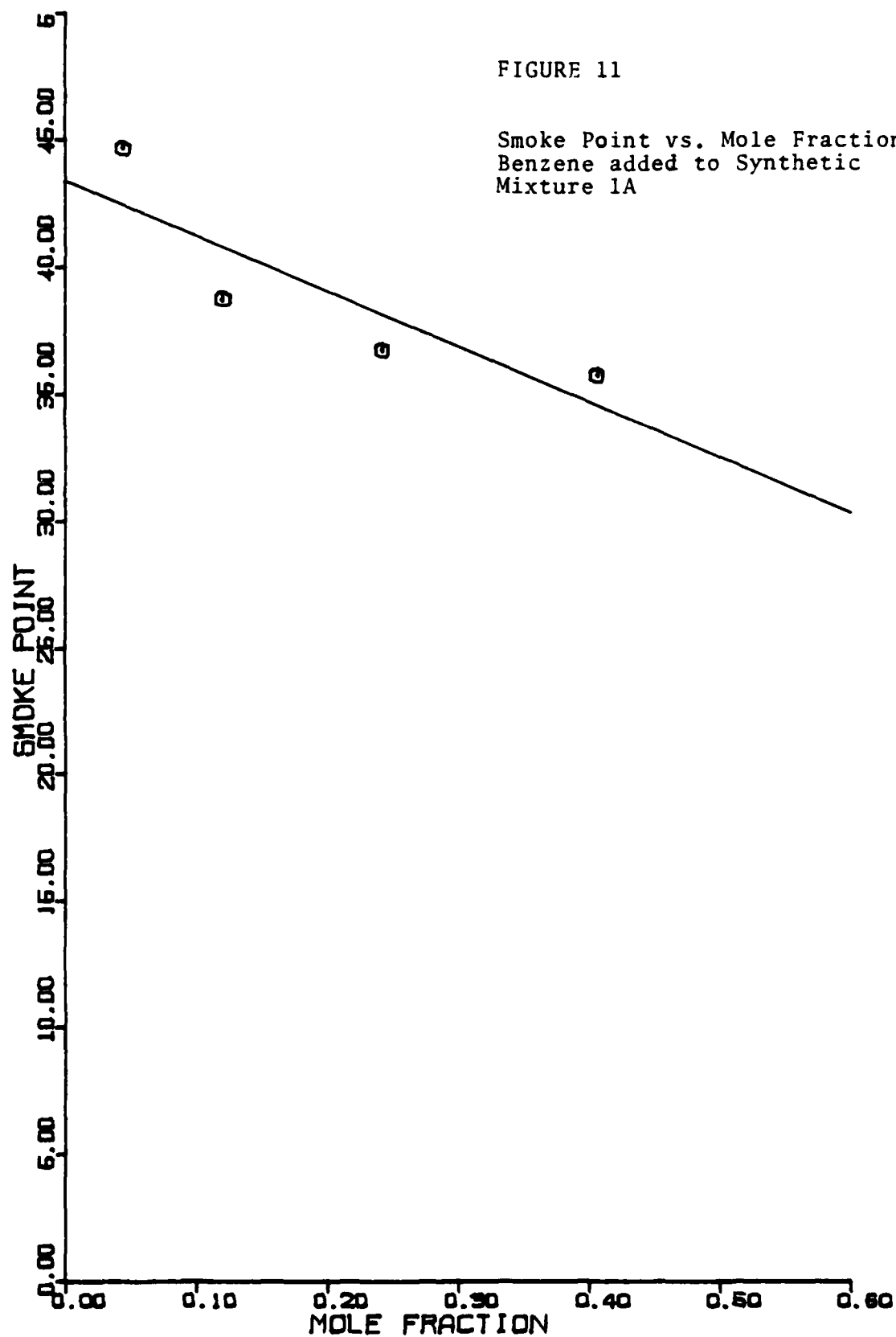


FIGURE 10

Smoke Point vs. Mole Fraction of
2-Hexene added to Synthetic
Mixture 1A

FIGURE 11

Smoke Point vs. Mole Fraction of
Benzene added to Synthetic
Mixture 1A



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FIGURE 12

Smoke Point vs. Mole Fraction of
Naphthalene added to Synthetic
Mixture 1

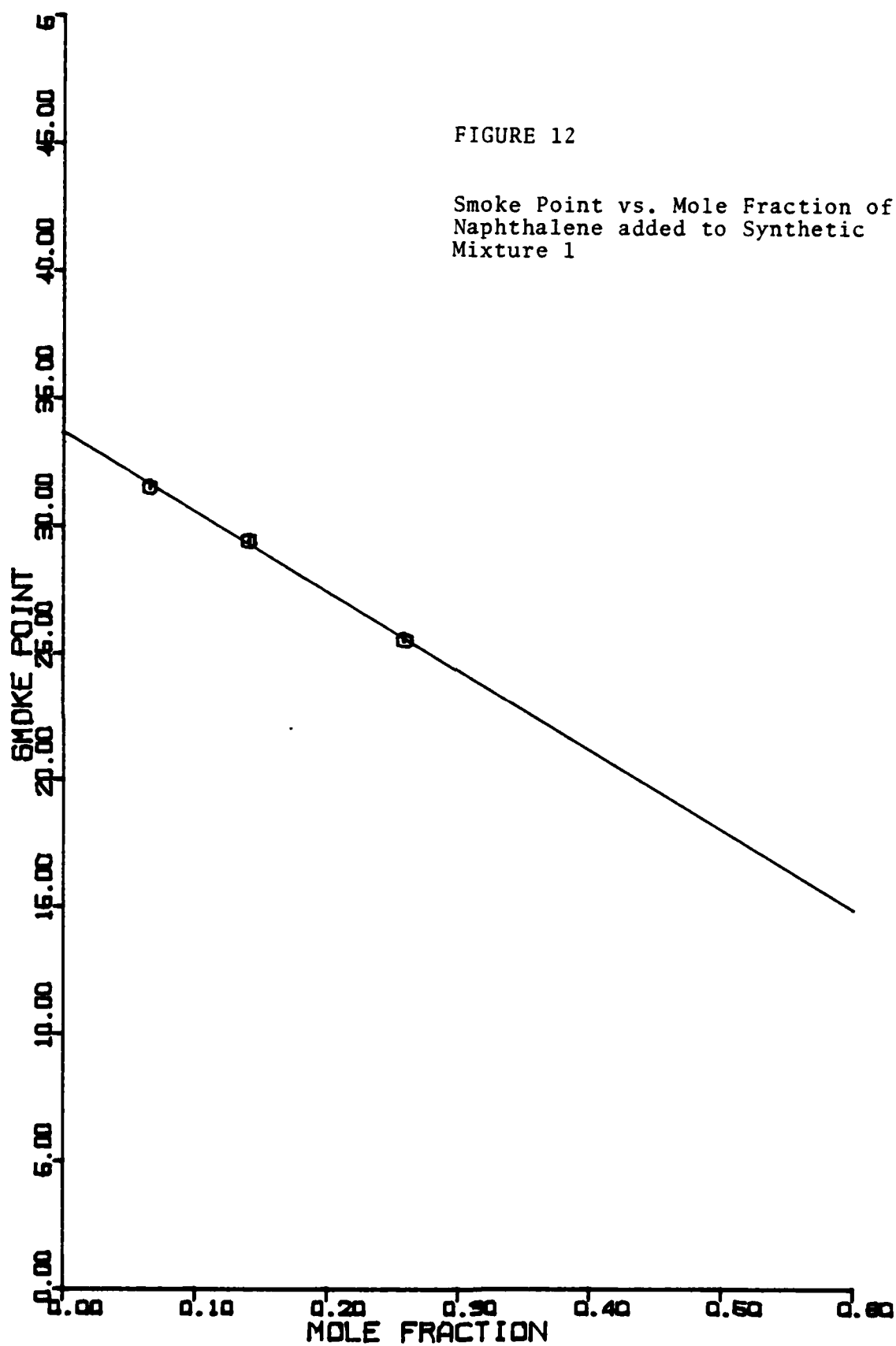


FIGURE 13

Smoke Point vs. Mole Fraction of
Toluene added to Synthetic Mixture
1A

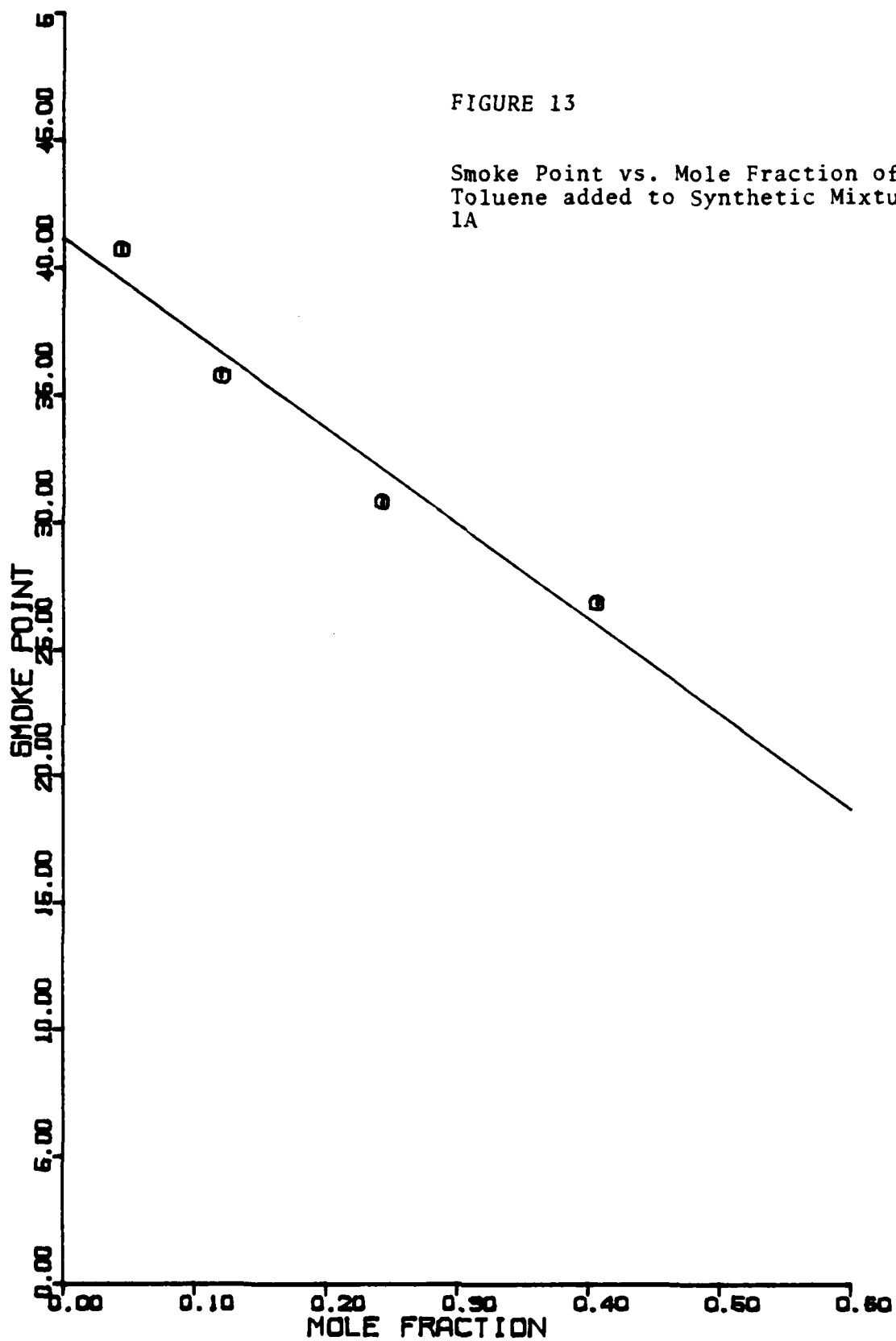


FIGURE 14

Smoke Point vs. Mole Fraction of
Cumene added to Synthetic Mixture
1A

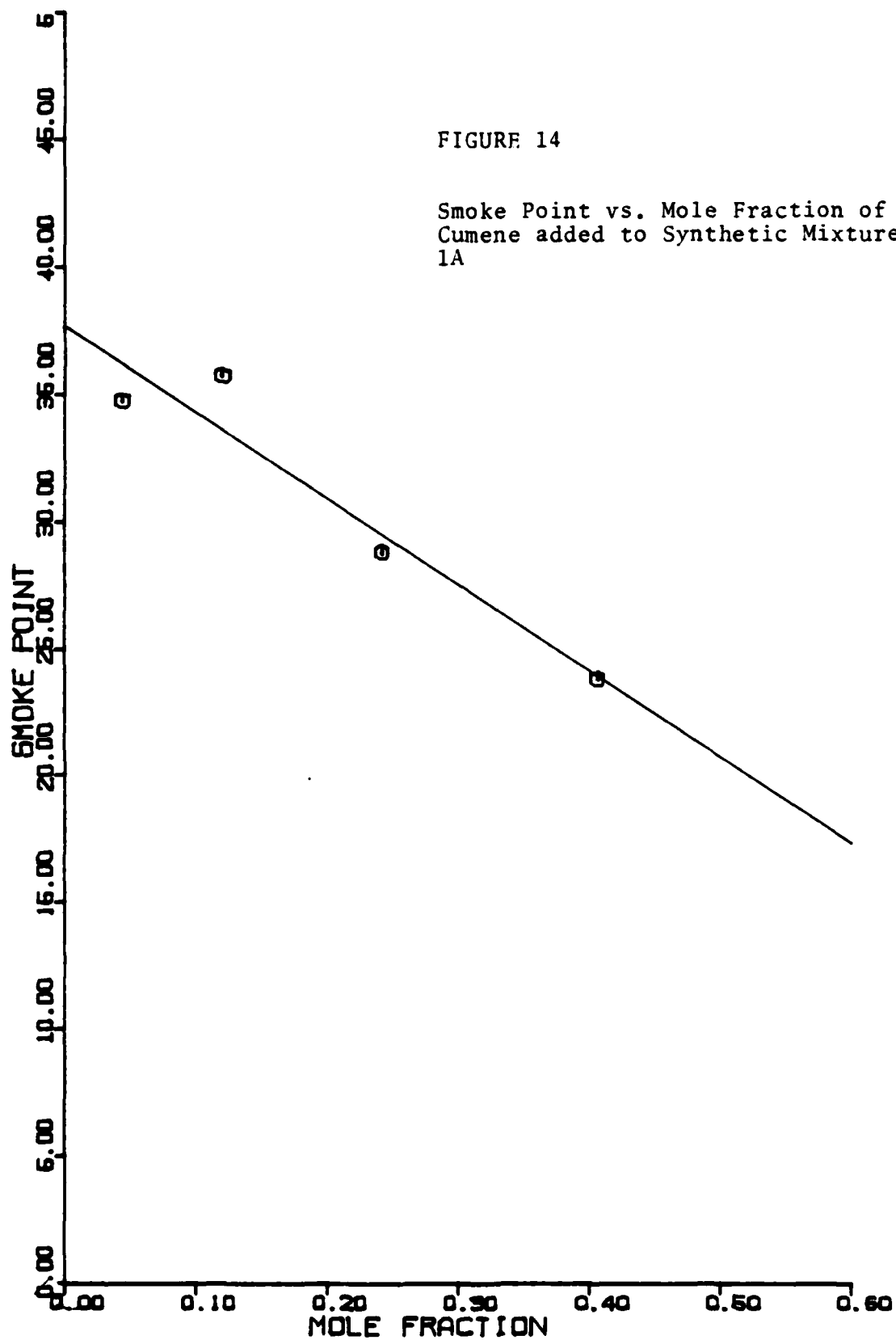


FIGURE 15

Smoke Point vs. Mole Fraction of
n-Butylbenzene added to Synthetic
Mixture 1

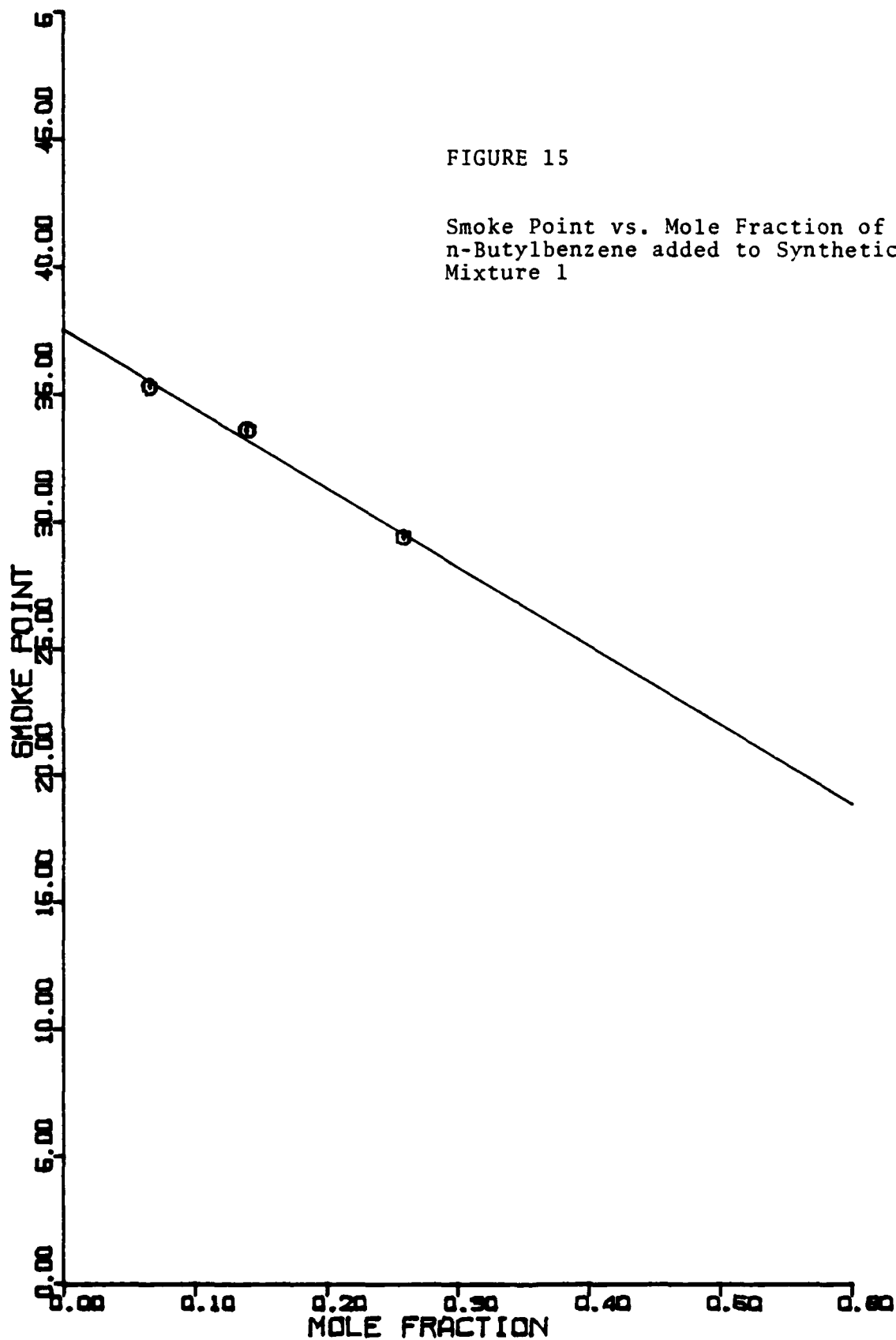


FIGURE 16

Smoke Point vs. Mole Fraction of
m-Xylene added to Synthetic Mixture 1

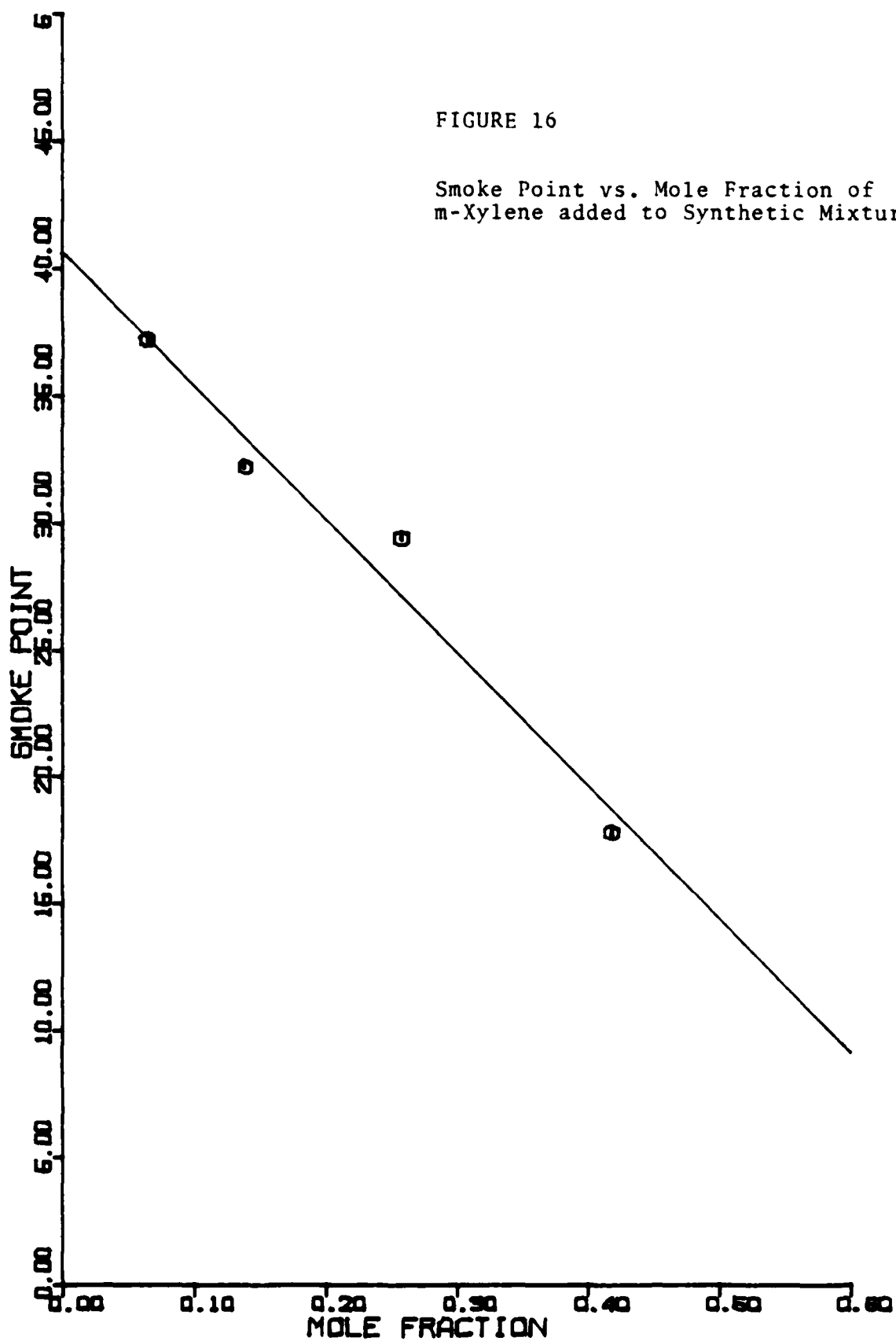


FIGURE 17

Smoke Point vs. Mole Fraction of
Tetralin added to Synthetic Mixture 1

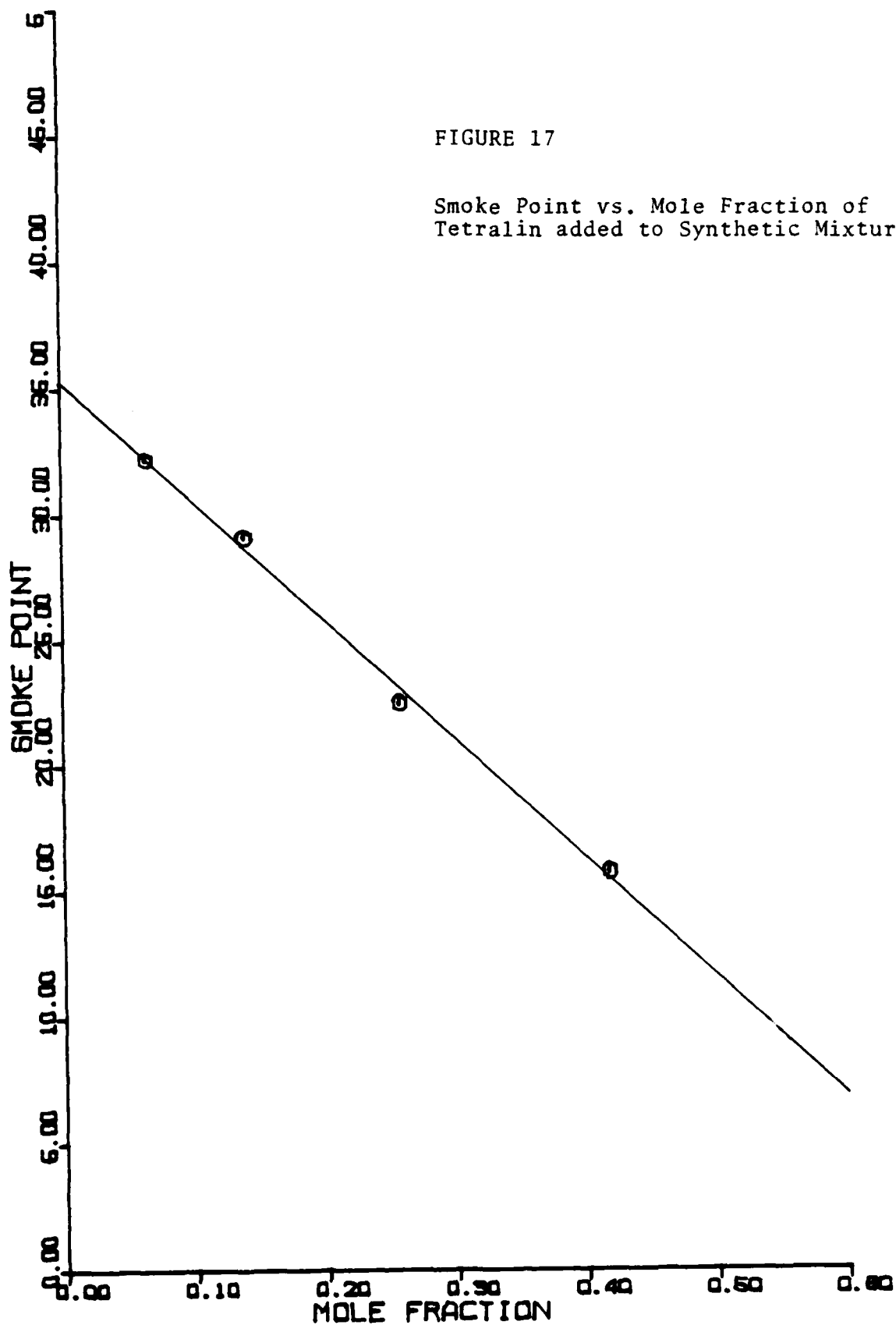
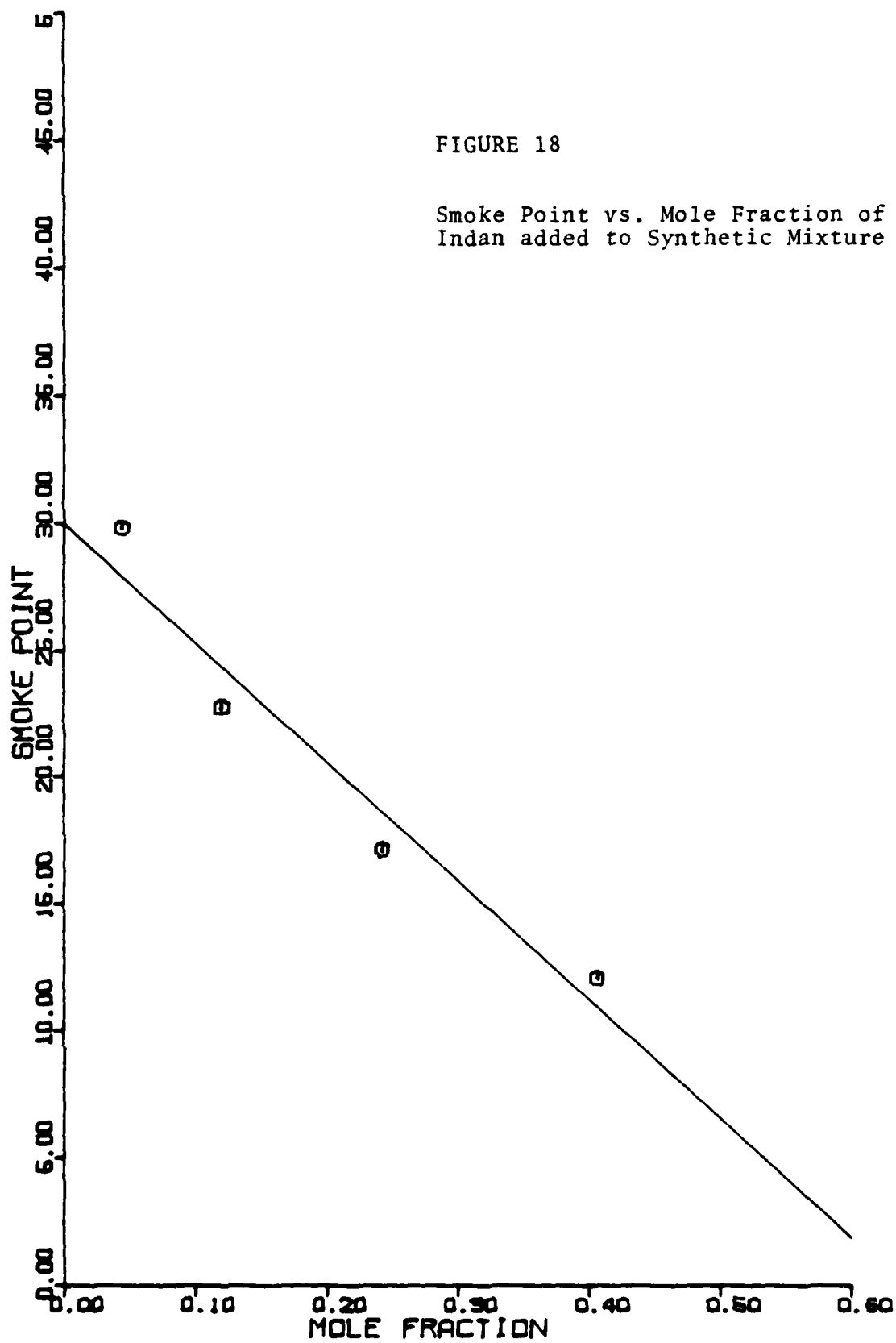


FIGURE 18

Smoke Point vs. Mole Fraction of
Indan added to Synthetic Mixture 1A



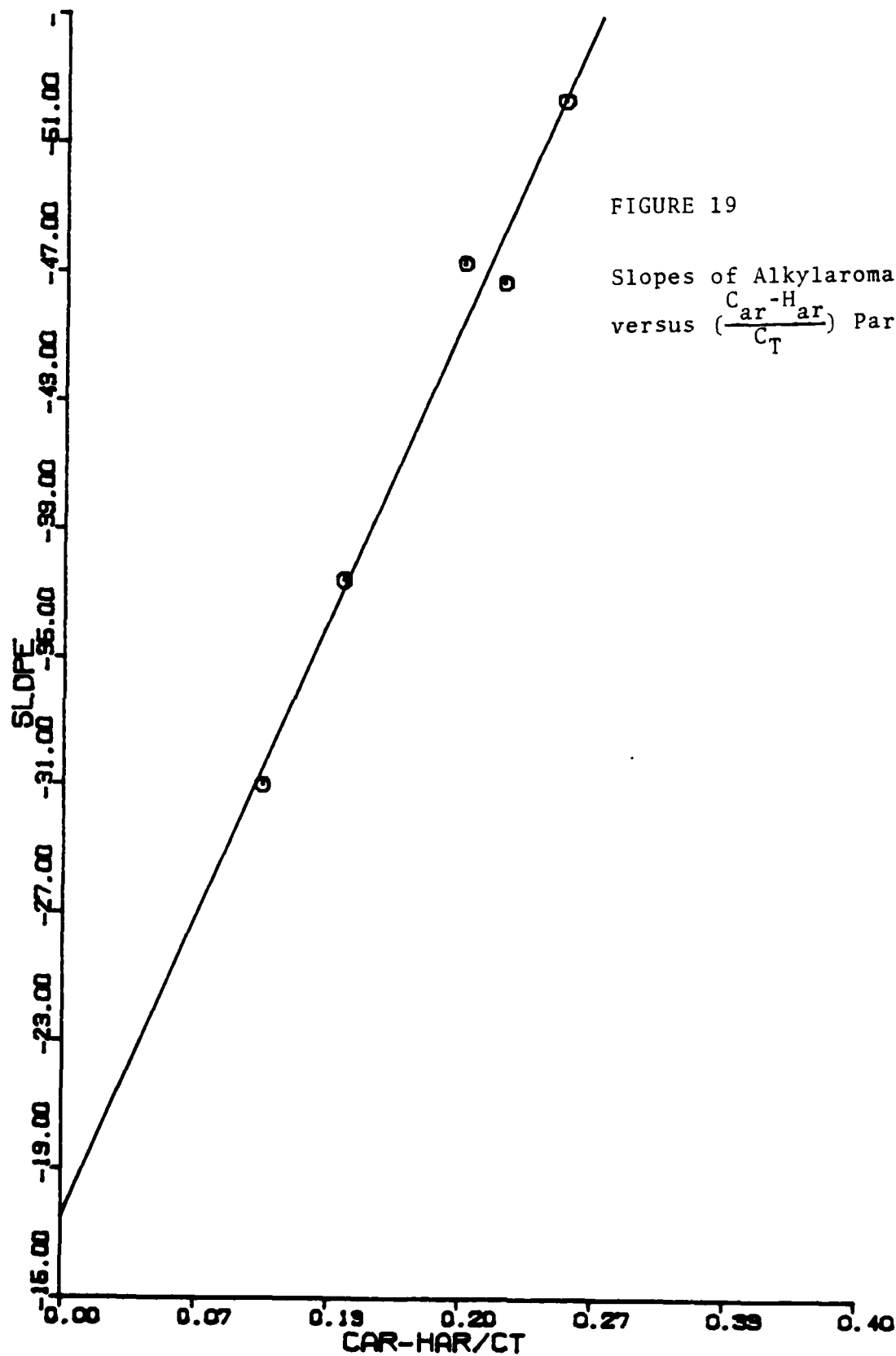


FIGURE 19

Slopes of Alkylaromatics
versus $\left(\frac{C_{ar} - H_{ar}}{C_T}\right)$ Parameter

FIGURE 20

Plot of Carbon Aromaticity (^{13}C NMR)
versus smoke points for Fuels 25-69

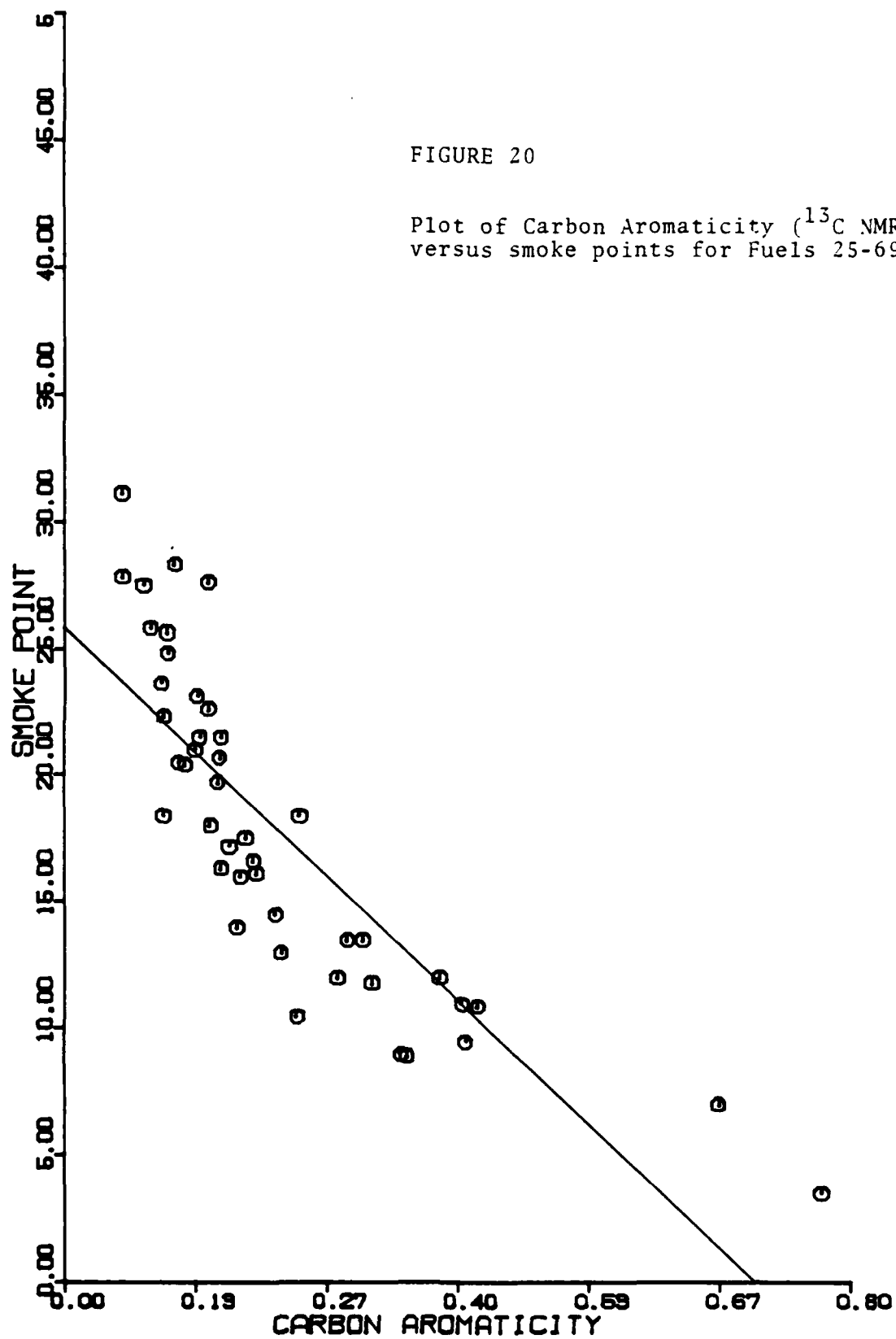


FIGURE 21

Plot of $\left(\frac{C_{ar}-H_{ar}}{C_T}\right)$ Parameter versus
smoke points for Fuels 25-69

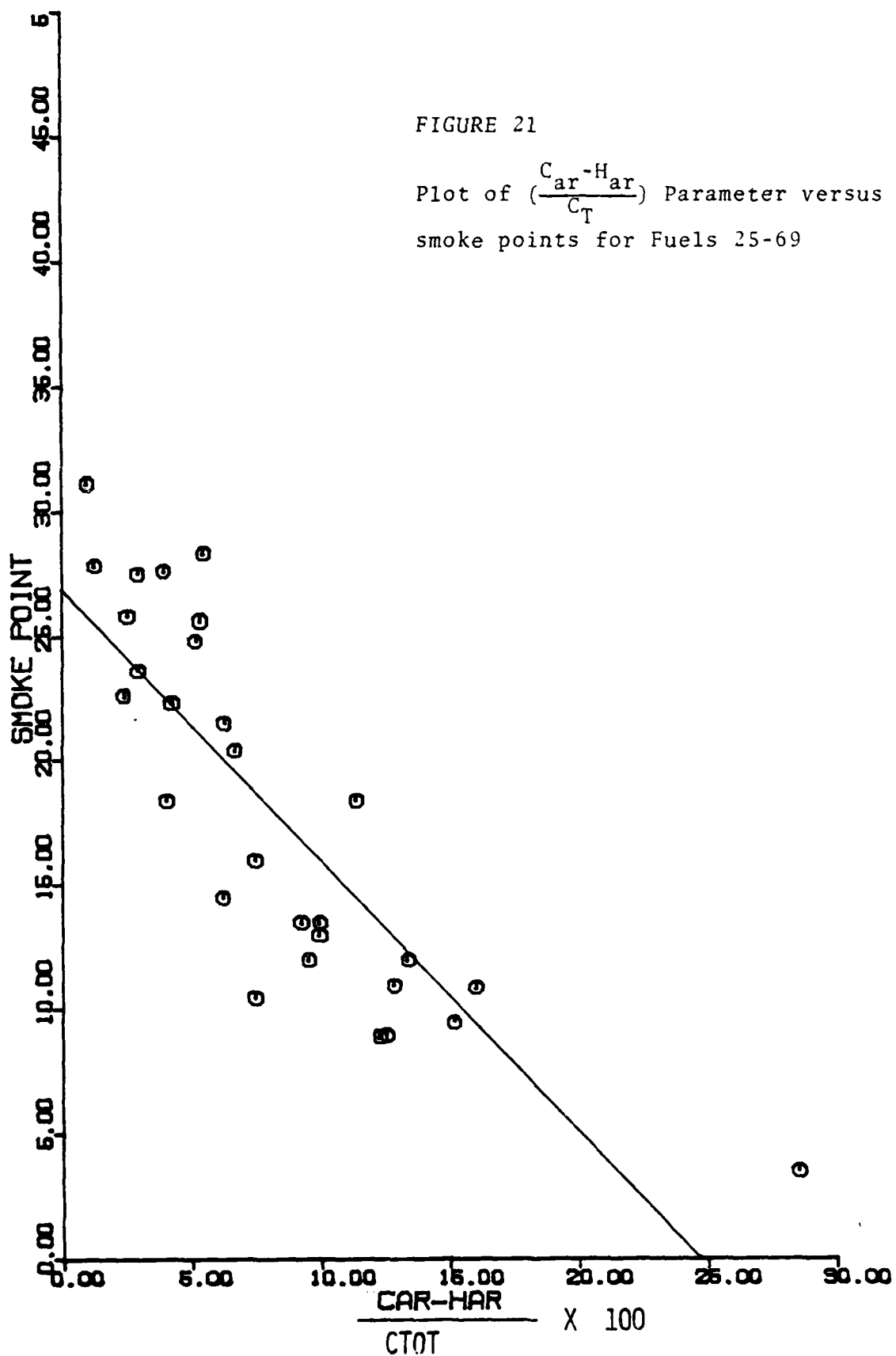
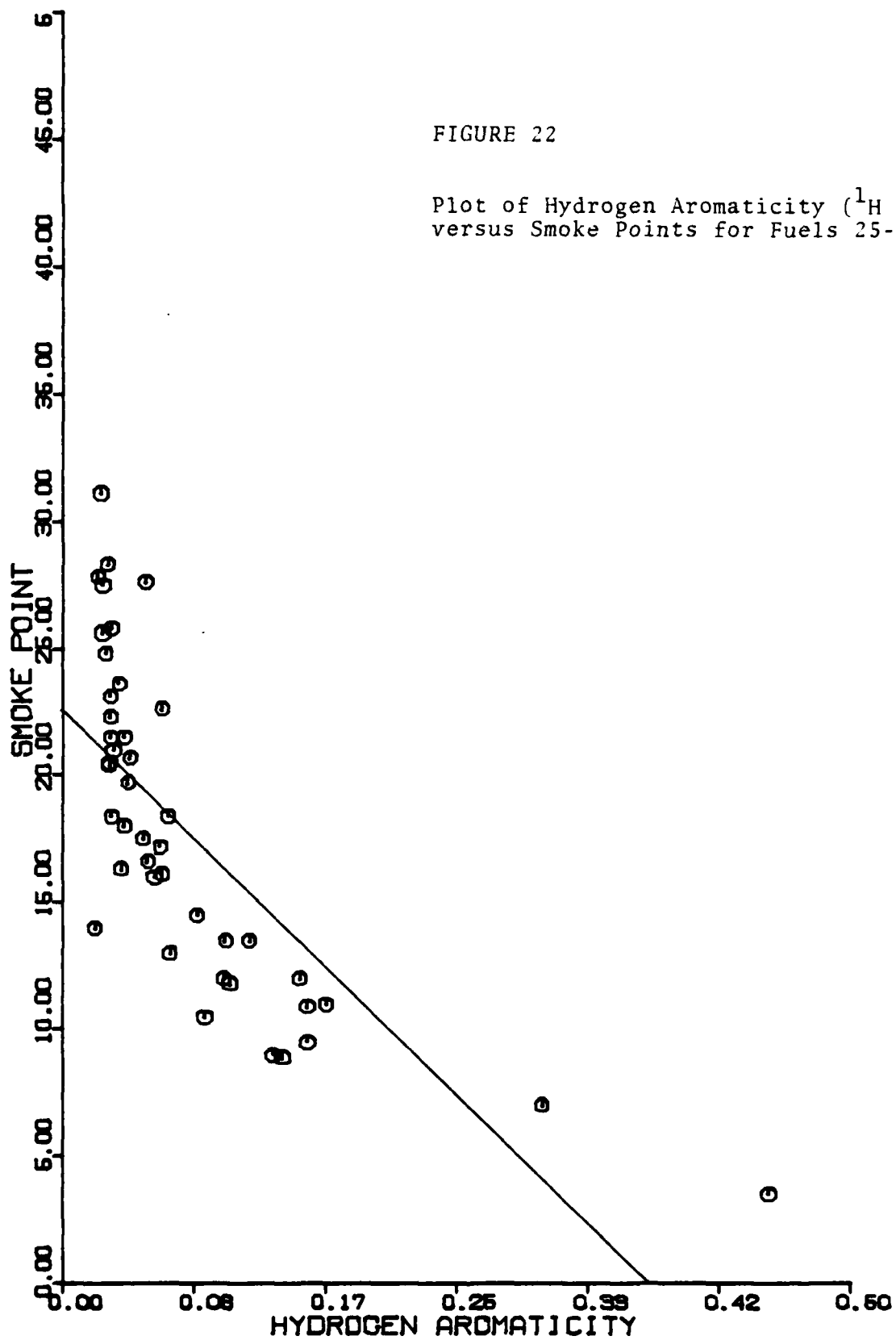


FIGURE 22

Plot of Hydrogen Aromaticity (^1H NMR)
versus Smoke Points for Fuels 25-69



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